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ADVANCED STIMULATED SCATTERING MEASUREMENTS
IN SUPERCRITICAL FLUIDS

(AFOSR Contract F49620-01-C-0020)

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SUMMARY/OVERVIEW
We are using stimulated scattering (stimulated Rayleigh, Brillouin, and Raman scattering) to study supercritical fluids. New diagnostics are needed in the supercritical regime because low pressure diagnostics do not work well. From our measurements we can determine thermal, compressional, and compositional properties of supercritical fuels *in situ*. These techniques should improve our knowledge of fluid properties in the supercritical state.

TECHNICAL DISCUSSION

Objectives

The objectives of this research are to develop stimulated scattering as a diagnostic for supercritical fluids, and use this technique to improve our understanding of fluids in the supercritical state.

The study of supercritical fluids and flows requires new diagnostic techniques. Currently available techniques such as laser-induced fluorescence (LIF) and coherent anti-Stokes Raman scattering (CARS) are complicated by increased molecular interactions, leading to stronger quenching, larger absorption and refractive index, and incomplete understanding of the influence of local conditions on spectroscopic parameters such as linewidths, nonresonant background contributions, and quenching rates. We believe that stimulated scattering techniques hold great promise for studying supercritical fluids.

Stimulated Scattering

Rayleigh, Brillouin, and Raman scattering occur commonly as spontaneous scattering. These scattering processes arise from natural oscillation modes of materials and can be used to determine the physical parameters responsible for those oscillations. When these collective modes are excited with a powerful laser, the mode oscillations can be driven so hard that they grow exponentially. In this case, the oscillations cause stimulated scattering. The dominant advantage of stimulated scattering is that the scattered signal can be made arbitrarily large; otherwise, these processes produce extremely weak signals. By using a probe to measure the induced amplification, we can obtain very good quantitative results. This technique is distinct from the stimulated scattering that builds up from noise, in which case quantification is very difficult.

The large signals from stimulated scattering are particularly helpful for investigating Rayleigh and Brillouin scattering, where the weak signals available from spontaneous scattering are difficult to discriminate from background excitation light. Other advantages of stimulated scattering include excellent temporal resolution, and improved spectral resolution and signal-to-noise ratio. Furthermore, the use of two laser beams allows spatial registration and point measurement of local conditions.

With a single detection system, all three processes—Rayleigh, Brillouin, and Raman— can be measured. These processes together provide measurements of a wide range of material properties. Rayleigh scattering provides information on thermal properties, Brillouin scattering

on compressional or elastic properties, and Raman scattering on chemical and compositional properties, density, and temperature. While spontaneous Brillouin and Raman scattering have been applied to supercritical fluids, the use of stimulated scattering for supercritical fluids is new.

Experiment

Stimulated scattering allows measurements of the physical properties of fuels, including compressibility, speed of sound, thermal diffusivity, and chemical composition, density, and temperature while at supercritical conditions. This is significant, because much work on supercritical fuels has been performed after returning the fuels to ambient conditions, rather than in the supercritical state. Our work complements well work on optical diagnostics of supercritical fuels being performed at Wright-Patterson using spontaneous Raman and fluorescence measurements.

Stimulated scattering measurements are performed by producing strong scattering interactions using a pump laser and then probing the scattering using a second probe laser. As a pump laser for our stimulated scattering measurements we use an injection-seeded Nd:YAG laser. The probe laser is a tunable diode laser. The pump laser sets up an electric polarization oscillating at the characteristic frequency of a scattering mode of the material.[1] For strong laser driving, this polarization acts as a driving force, leading to amplification of both the material oscillation and the scattered optical wave. The optical amplification is detected as a gain or loss on the probe beam. Spatial resolution is determined by the overlap volume of the pump and probe beams.

We have previously reported the design and construction of a cell for capable of operation up to 600 K and 2000 psi. In design of that cell, we have drawn on information gained from conversations with Tim Edwards and Chris Bunker of AFRL–Wright-Patterson in their work on high pressure / high temperature systems. We have subsequently made a number of modifications to this cell. To avoid leaks at high temperatures, we substituted titanium bolts for the steel bolts, and glass windows for the fused silica windows. Titanium and glass have nearly the same thermal expansion coefficient. When operating the cell at high temperature, we found that convection near the windows caused beam wander, particularly in the region of the critical point. To minimize these effects, we have shortened the cell to an internal length of 2.5 cm.

We have used the modified cell to perform stimulated scattering measurements in the supercritical and near critical regimes. These are the first stimulated Rayleigh and stimulated Brillouin scattering at supercritical conditions to our knowledge. An example of measurements performed at 200 C and 630 psi is shown in Fig. 1. The abscissa is the difference in frequency between the pump and probe lasers determined by the wavemeter. The gain signal is divided by the pump and probe laser intensities to compensate for intensity fluctuations in each laser. The outer two peaks are Brillouin peaks; the central pair of peaks is due to stimulated Rayleigh scattering. The positive-going Brillouin peak to the left is a gain peak, corresponding to transfer of power from the Nd:YAG laser to the probe laser. The negative-going peak to the right is a loss peak, wherein power is transferred from the probe laser to the pump laser.

We performed fits to the measured lineshapes to determine linewidths, lineshifts, and peak heights. The electrostrictive Brillouin lineshape is described by the real part of the complex Lorentzian profile; the thermal Brillouin and Rayleigh lineshapes are described by the imaginary parts of a complex Lorentzian profile.[2] The measured lineshapes are given by the convolution of the Gaussian spectral lineshape of the Nd:YAG pump laser with these Lorentzian profiles. These convolved lineshape may be expressed as the real and imaginary parts of the complex error function for the Brillouin and Rayleigh peaks, respectively (the former is a Voigt profile). Complex error function fits to the data were performed using the algorithm of Humlicek,[3,4] and the Igor graphics program (WaveMetrics, Inc.). We used the Fourier-transform limited linewidth calculated from pulsewidth as the spectral linewidth of the pump laser. To eliminate the contribution of the 10 Hz dither used to lock the Nd:YAG laser to the seed laser, measurements were performed at 5 Hz. The seed laser linewidth is specified to be less than 300 kHz in 50 ms.
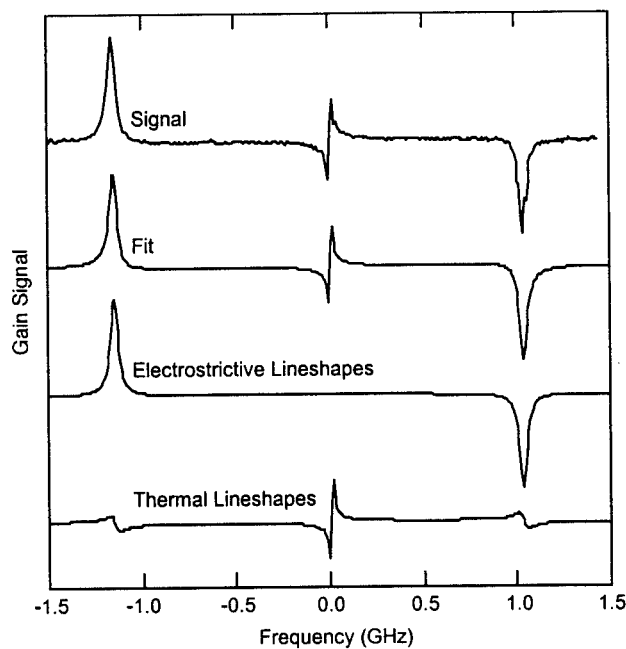
Fig. 1. Stimulated Rayleigh and Brillouin spectrum for hexane at 200°C and 630 psi.
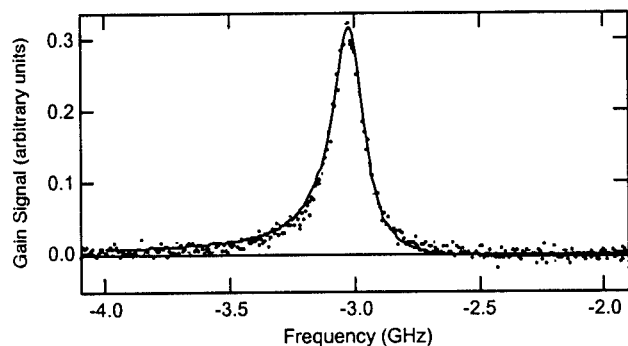

Fig. 2. Data (points) and fit (solid line) for stimulated Brillouin gain peak for n-hexane at 1064 nm. Stimulated thermal Brillouin scattering gives an asymmetry to the peak.
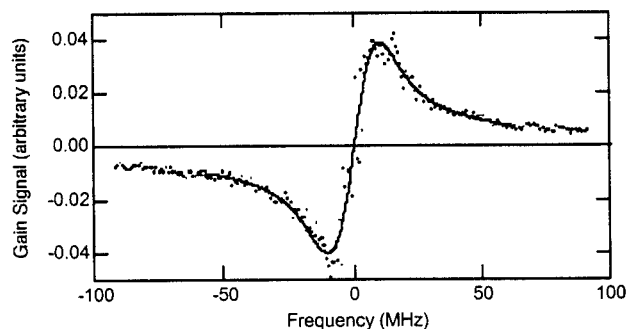

Fig. 3. Data (points) and fit (solid line) for stimulated thermal Rayleigh scattering in n-hexane at 1064 nm.
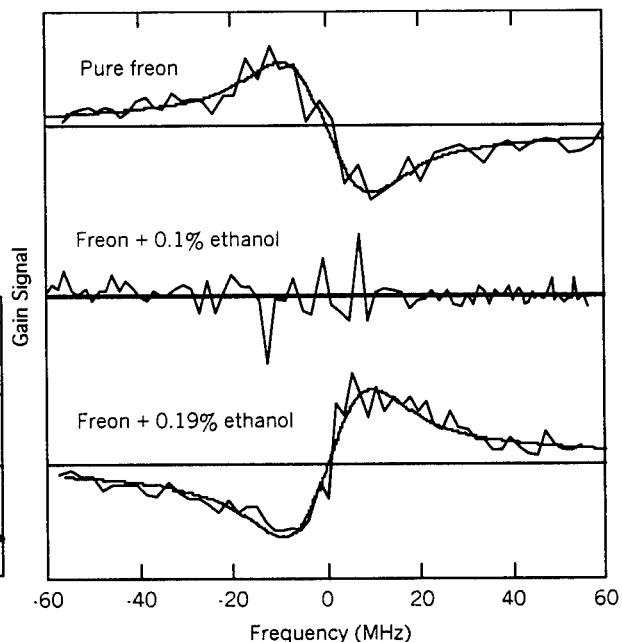

Fig. 4. Measured stimulated Rayleigh gain signal (solid curve) and fitted profile (dashed curve) in pure freon 113 (top), and freon with 0.1% ethanol (middle) and 0.19% ethanol (bottom).

Table 1.

Properties measured in hexane using stimulated Rayleigh /Brillouin scattering at 1064 nm.

Property	Our Results	Literature Values
Brillouin shift	2.91±0.06 GHz	
Brillouin width	151±8 MHz	
Rayleigh width	7.9±3.2 MHz	
Ratio of electric to absorptive coupling constants	8.8±0.6	
Acoustic damping time	1.06 ns	
Acoustic velocity	1.14 km/s	1.10 km/s
Acoustic attenuation coefficient	8.3×10^5 m^{-1}	7.4×10^5 m^{-1}
Effective mass diffusion coefficient	7.4×10^{-6} m^2/s	
Isentropic compressibility	1.2×10^{-9} m^2/N	
Thermal diffusivity	9.6×10^{-8} m^2/s	9.2×10^{-8} m^2/s

The full fit to the Rayleigh/Brillouin spectrum is shown as the curve labeled "fit" in Fig. 1. Very good agreement is found between the measured and fit lineshapes (see also Figs. 2 and 3). The electrostrictive and thermal contributions to the overall fit are shown separately at the bottom of Fig. 1. The thermal scattering is due to absorption by OH or CH overtone or combination bands. This absorption increases the size of the stimulated Rayleigh peak (it is otherwise difficult to observe) and causes an asymmetry in the stimulated Brillouin peak due to the imaginary Lorentzian shape of the thermal Brillouin scattering.

Expanded spectra for stimulated Brillouin and stimulated Rayleigh scattering in hexane at room temperature are shown in Figs. 2 and 3. Also shown are fits to these spectra. The frequency values for the stimulated Rayleigh peak in Fig. 3 were determined from the heterodyne signal between the seed and probe lasers. This peak is quite narrow. The average linewidth determined from multiple fits such as shown in Fig. 3 gives value of 7.9±3.2 MHz, which is in good agreement with the value expected from the thermal diffusivity for n-hexane. These measurements were performed with a pulsewidth for the Nd:YAG laser of approximately 30 ns, which corresponds to a full width half maximum spectral linewidth of about 15 MHz. Thus the laser linewidth is about twice the measured linewidth of the Rayleigh peak. The good agreement with the expected linewidth confirms that the Nd:YAG laser has a transform-limited linewidth of 15 MHz. The spectroscopic and thermodynamic properties for n-hexane determined from numerous such fits are given in Table 1. The errors are standard deviations of values averaged from 14 or more measurements. These calculations use the refractive index for hexane (extrapolated to 1064 nm from a literature expression[5]) as appropriate.[2] Good agreement is obtained with values available in the literature.

We have observed electrostrictive stimulated Rayleigh scattering in a liquid and created a transition to stimulated thermal Rayleigh scattering with the addition of an absorbing liquid. With the proper amount of absorption, the electrostrictive and thermal contributions to the scattering exactly cancel, resulting in no stimulated Rayleigh scattering. This effect is shown in Fig. 4. The top curve shows a pure electrostrictive stimulated Rayleigh peak in pure freon 113. With an addition of 0.1% ethanol (an absorption coefficient of 0.00012 cm^{-1}) the stimulated thermal scattering cancels the stimulated electrostrictive scattering (center curve). With addition of more ethanol, the stimulated peak has flipped over (bottom curve)

We are currently investigating fluctuations near the critical point. These fluctuations can cause flow and pressure instabilities, which have been found to have destructive effects on tubing.[6,7] Avoiding these fluctuations is very important for fuel systems that transition into the supercritical regime.

REFERENCES

1. G.W. Faris, L.E. Jusinski, and A.P. Hickman, "High-resolution stimulated Brillouin gain spectroscopy in glasses and crystals," J. Opt. Soc. Am. B 10, 587-599 (1993).

2. W. Kaiser and M. Maier, "Stimulated Rayleigh, Brillouin, and Raman spectroscopy," in *Laser Handbook*, F. T. Arecchi and E. O. Schulz-Dubois, Eds. (North-Holland, Amsterdam, 1972), Vol. 2, pp. 1077-1150.

3. J. Humlicek, "Optimized computation of the Voigt and complex probability functions," J. Quant. Spectrosc. Radiat. Transfer 27, 437-444 (1982).

4. F. Schreier, "The Voigt and complex error function: A comparison of computational methods," J. Quant. Spectrosc. Radiat. Transfer 48, 743-762 (1992).

5. H. El-Kashef, "Molecular properties of hexane," J. Modern Opt. 46, 1389-1399 (1999).

6. W.S. Hines and H. Wolf, "Pressure oscillations associated with heat transfer to hydrocarbon fluids at supercritical pressures and temperatures," ARS Journal , 361-366 (March 1962).

7. L.E. Faith, G.H. Ackerman, and H.T. Henderson, Heat sink capability of jet A fuel: Heat transfer and coking studies, NASA Report No. CR-72951 (1971).